Constituents of Umbelliferous Plants

XIV.* Coumarins of *Peucedanum oreoselinum* (L.) Moench

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The fruits of *Peucedanum oreoselinum* (L.) Moench, in addition to athamantin (I) and oroselol (II), afforded 8(*S*),9(*R*)-9-acetoxy-*O*-senecioyl-8,9-dihydrooroselol (III), 8(*S*),9(*R*)-9-acetoxy-*O*-isovaleryl-8,9-dihydrooroselol (IV), 8(*S*),9(*R*)-9-hydroxy-*O*-senecioyl-8,9-dihydrooroselol (V), 8(*S*),9(*R*)-9-isovaleryloxy-8,9-dihydrooroselol (VI), and 8(*S*)-*O*-senecioyl-8,9-dihydrooroselol (VII).

The root afforded (I), (II), (IV), and 8(*S*)-*O*-isovaleryl-8,9-dihydrooroselol (VIII).

Identity between (III) and peucenidin, and between (VI) and vaginidin is established. The structures (X) [4,5] and (XV) [8,9] previously assigned to peucenidin and vaginidin, respectively, are revised accordingly.

Peucedanum oreoselinum (L.) Moench has previously been an object of chemical investigation. In 1844, Schnedermann and Winckler [1] isolated a compound from the root, which they named athamantin. For this compound Späth and Schmid [2] in 1940 proposed two structural possibilities, one of which (I), was later proved to be correct by Halpern *et al.*[3] These authors also tentatively assigned the relative configuration *cis* to athamantin. Furthermore, oroselol (II) was obtained from the root.
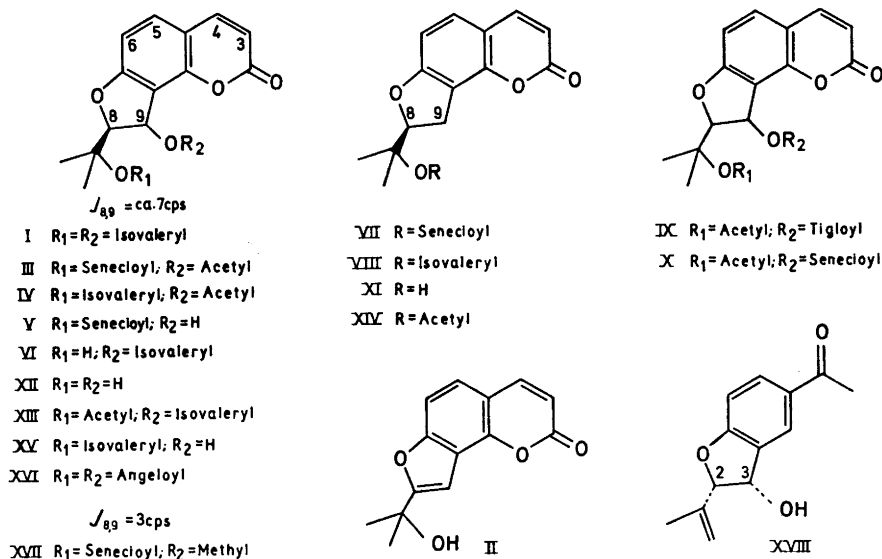
More recently Prokopenko [4] isolated a coumarin, peucenidin, from the fruits, to which the structure (IX) was assigned. In a subsequent paper,[5] however, the revised structure (X) was stated for peucenidin, this revisal being based solely on a study of the ¹H NMR-spectrum.

In our hands, a coumarin fraction, obtained from the fruits afforded, in addition to oroselol, three groups of dihydrofurocoumarins.

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* Presented at the *3rd Nordic Symposium on the Chemistry of Natural Products*, Ørsta, Norway, June 1969.

Part XIII. *Acta Chem. Scand.* **24** (1970) 2863.

The first of these is composed of monoesters derived from the known alcohol 8(*S*)-8,9-dihydroorooselol (XI). The ^{1}H NMR-spectra of appropriate chromatographic fractions revealed the presence of the senecioate (VII) and the isovalerate (VIII). They were virtually inseparable by chromatography,

$J_{8,9}$ = ca. 7 cps

I $R_1 = R_2 =$ Isovaleryl

III $R_1 =$ Senecloyl; $R_2 =$ Acetyl

IV $R_1 =$ Isovaleryl; $R_2 =$ Acetyl

V $R_1 =$ Senecloyl; $R_2 =$ H

VI $R_1 =$ H; $R_2 =$ Isovaleryl

XII $R_1 = R_2 =$ H

XIII $R_1 =$ Acetyl; $R_2 =$ Isovaleryl

XV $R_1 =$ Isovaleryl; $R_2 =$ H

XVI $R_1 = R_2 =$ Angeloyl

$J_{8,9}$ = 3 cps

XVII $R_1 =$ Senecloyl; $R_2 =$ Methyl

VII   R = Senecloyl

VIII   R = Isovaleryl

XI   R = H

XIV   R = Acetyl

IX $R_1 =$ Acetyl; $R_2 =$ Tigloyl

X $R_1 =$ Acetyl; $R_2 =$ Senecioyl

II

XVIII

and fractional crystallization only afforded the senecioate (VII) in a pure state. The identity of (VII) was ascertained by synthesis from authentic 8(*S*)-8,9-dihydrooroselol (XI). Recently Bohlmann and Grenz [6] isolated compound (VII) from the root of *Ligusticum pyrenaicum* Koch.

The second group of dihydrofurocoumarins consisted of diesters of an unknown alcohol 8(*S*)-9-hydroxy-8,9-dihydrooroselol (XII). In addition to athamantin (I), which was identified by comparison with an authentic sample, two other crystalline coumarins (III) and (IV) were obtained. From the ^{1}H NMR-spectrum of (III) its close relationship with athamantin (I) was evident, all differences in the spectra being attributable to the presence of an acetyl and a senecioyl group in stead of two isovaleryl groups. Hydrogenolysis of the benzylic ester function and concomitant hydrogenation of the double bond of the senecioyl group afforded 8(*S*)-*O*-isovaleryl-8,9-dihydrooroselol (VIII). The identity of (VIII) was established by its synthesis from the alcohol (XI). This evidence established the structure 8(*S*)-9-acetoxy-*O*-senecioyl-8,9-dihydrooroselol for compound (III), and in an analogous way the structure 8(*S*)-9-acetoxy-*O*-isovaleryl-8,9-dihydrooroselol for compound (IV). With platinum oxide as a catalyst in the hydrogenolysis reaction, saturation of the double bond of the pyrone ring was remarkably suppressed, and fairly good yields of the dihydrooroselol esters were obtained. This kind of selectivity was not observed, when palladium on carbon was used.

Recently Bohlmann and Grenz [6] isolated a coumarin from the root of *Ligusticum pyrenaicum*, for which the constitution (III) was established, yet without specification of the absolute configuration at C-8. The optical rotation values and other physical data confirm identity with (III). In addition, Bohlmann and Grenz [6] obtained a non-crystalline and poorly characterized coumarin, to which the constitution (IV) was assigned in analogy with compound (III).

Compound (III) was found to be the major coumarin constituent of the fruits, whereas a compound differing from (III) by interchange of the ester groups was not obtained. Peucenidin (X), to which the latter structure was assigned,[4,5] shows striking similarities to compound (III), with regard to physical data. Mild methanolic saponification of peucenidin (X) and isolation of oroselol acetate from the complex reaction mixture was the observation, on which allocation of the ester group positions was based by Prokopenko.[4] As expected, thin-layer chromatographic examination of a reaction mixture obtained in a similar way from coumarin (III), did not reveal the presence of oroselol acetate. This compound was obtained from oroselol (II) by acetylation according to Oppenauer;[7] the acetylation method employed by Prokopenko afforded unchanged starting material in our hands.*

The third group of dihydrofurocoumarins is represented by the two monoesters (V) and (VI), derived from the coumarin alcohol (XII). For the monoester (V) the structure 8(*S*)-9-hydroxy-*O*-senecioyl-8,9-dihydrooroselol was established by the identity of its acetylation product with compound (III). The acid moiety of the monoester (VI) was shown to be isovaleric acid by ^{1}H NMR-spectroscopy. As opposed to compound (V), the monoester (VI) was difficult to acetylate, except when the method devised by Oppenauer,[7] for acylation of tertiary alcohols was used. The acetylation product was different from compound (IV), but their ^{1}H NMR-spectra were almost identical. A microscale hydrogenolysis of the acetylation product (XIII) and thin-layer chromatography of the reaction mixture revealed that the acetate (XIV), and not the isovalerate (VIII) had been formed. Hydrogenolysis of the monoester (VI) on a preparative scale afforded 8(*S*)-8,9-dihydrooroselol (XI). This evidence established the structure 8(*S*)-9-isovaleryloxy-8,9-dihydrooroselol for compound (VI). Information about which hydroxyl group is left unesterified in the monoesters (V) and (VI), can also be obtained from a comparison of their ^{1}H NMR-spectra with those of their acetylation products (III) and (XIII), respectively. The acylation shifts observed for the protons H(8) (high field signal) and H(9) (low field signal) of the dihydrofuran ring, are conceivable only with the free hydroxyl group being situated at C(9) in compound (V) and in the side chain in compound (VI).

From *Selinum vaginatum* Seshadri *et al.*[8] recently isolated vaginidin, a coumarin to which the structure (XV) was assigned. The reported ^{1}H NMR-spectrum is identical with that obtained from compound (VI); again, melting points and IR-spectral data are very similar. Optical rotation values were

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* After dispatch of the manuscript a sample of authentic peucenidin was kindly provided by Dr. A. P. Prokopenko.

This sample and compound (III) afforded identical IR-spectra (KBr-pellets) and hydrogenolysis products (TLC). Accordingly the structure of peucenidin is revised from (X) to (III).

not reported for vaginidin, but in a later paper [9] its chemical conversion into
8(S)-tetrahydrooroselol is mentioned without experimental data. This estab-
lishes the identity of vaginidin with compound (VI). The structure previously
assigned to vaginidin must be revised accordingly. The basis on which Seshadri
et al. concluded that the free hydroxyl group in vaginidin was situated at C-9,
was mainly the acylation shift observed in the ^{1}H NMR-spectrum for the
dihydrofuran proton resonating at highest field. This proton was incorrectly
considered to be H(9). The acylation shift was derived by comparison with
the ^{1}H NMR-spectrum of archangelicin (XVI).[10]

An extract obtained from the root of *Peucedanum oreoselinum* (L.) Moench
was worked up in a way much similar to that described for the fruit extract.
In addition to oroselol (II) the dihydrofurocoumarins athamantin (I), 8(S)-O-
isovaleryl-8,9-dihydrooroselol (VIII), and 8(S)-9-acetoxy-O-isovaleryl-8,9-
dihydrooroselol (IV) were obtained.

For all the coumarins shown to be derived from 8(S)-9-hydroxy-8,9-
dihydrooroselol (XII), the configuration at C-9 deserves comment. Their
8(S) configuration is evident from their relationship with 8(S)-8,9-dihydro-
oroselol (XI), which was earlier correlated with (−)-tubaic acid [11] (see also
Ref. 12). Furthermore, they all possess identical relative configurations, as
coupling constants $J_{8,9} = 6 - 7$ cps are consistently observed in all ^{1}H NMR-
spectra. For athamantin (I), *cis*-configuration of the dihydrofuran protons
was suggested by Halpern *et al.*[3] on the basis of the high thermostability of
athamantin (I), as compared to the remarkable ease with which both iso-
valerate groups are eliminated by acid catalysis. This suggestion is widely
accepted [6,11,12] and generally considered to be consistent with the coupling
constant $J_{8,9} = 6 - 7$ cps. In accordance with this view, the configuration
8(S), 9(R) was earlier assigned to athamantin and archangelicin [11]* and might
similarly be assigned to the coumarins (III), (IV), (V), and (VI).

In compound (XVII), which was obtained by mild methanolysis [6] of
compound (III), and to which the relative configuration *trans* was assigned,
the epimeric nature in relation to athamantin (I) is evident from the coupling
constant $J_{8,9} = 3$ cps.

The expectation of $J_{cis-2,3}$ being larger than $J_{trans-2,3}$ in 2,3-dialkyl-2,3-
dihydrobenzofurans has been verified experimentally.[13] In contrast, Zalkow
and Ghosal [14] for the isomeric series of 2,3-dihydrobenzofurans carrying an
isopropyl group at C-2 and an oxygen substituent at C-3 reported the
unusual coupling constants $J_{trans-2,3} = 6$ cps and $J_{cis-2,3} = 4$ cps. Dihydrotoxol
($J_{2,3} = 4$ cps) was a member of one of these series and the allocation of stereo-
chemistry was based on the degradation of the related compound toxol (XVIII)
to (+)-tartaric acid by exhaustive ozonolysis.[15] In view of this report, the
assignment of *cis*-configuration and accordingly 9(R) configuration to
athamantin (I) and the related coumarins mentioned above, must be considered
questionable.

However, the possibility of an epimerization taking place at C-3 during
ozonolysis of toxol (XVIII), can hardly be ruled out. In the authors' opinion,
therefore, it is not possible, solely on these grounds to decide, whether

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* Unfortunately this configuration was erroneously designated 8(S), 9(S) in the paper cited.

athamantin (I) and its congeners should be given the configuration 8(S), 9(S) or 8(S), 9(R).*

EXPERIMENTAL

The silica gel (Merck, 0.05 — 0.20 mm) used for column chromatography, was activated at 120° overnight, after which 10 % of water was added. The melting points are corrected and were determined in capillary tubes in an oil bath. The ^{1}H NMR-spectra were obtained at 60 Mc/s on a Varian V — 4 300 or a Jeol JNM — C — 60HL instrument. The IR-spectra were recorded using the KBr-technique, on a Perkin-Elmer grating IR-spectrophotometer, Model 457. Microanalyses were performed by Dr. A. Bernhardt, Elbach über Engels-kirchen.

The plant material was collected in September at the Southern coast of Sweden.

Isolation of the coumarin mixture from the fruits. Extraction of the dried and ground fruits (1400 g) with ether and subsequent evaporation of the solvent afforded 253 g of oily extract. After dilution with 90 % methanol the extract was defatted by extraction with petroleum ether.

Gross fractionation on silica gel columns, with benzene, benzene-chloroform mixtures, chloroform, and chloroform-methanol mixtures as the eluents, divided the defatted extract (43 g) into four main fractions A, B, C, and D, mentioned in the order eluted.

Fraction A after several crystallizations from ether-petroleum ether yielded 8(S)-O-senecioyl-8,9-dihydrooroselol (VII), m.p. 80.5 — 82° (Ref. 6, m.p. 79°), $[\alpha]_D^{20}+303°$ (c 0.3, CH_3OH). The analytical data were concordant with the composition $C_{19}H_{20}O_5$. The IR-spectrum was identical with that of the sample, prepared from authentic 8(S)-8,9-dihydrooroselol (XI) by acylation with senecioic anhydride.

Fraction B. Athamantin (I), m.p. 54 — 56° (Ref. 2, m.p. 58 — 60°), $[\alpha]_D^{20}+100°$ (c 0.6, CH_3OH) (Ref. 3, $[\alpha]_D^{21}+102°$ (c 0.6, CH_3OH)). The IR-spectrum was identical with that of an authentic sample, and the ^{1}H NMR-spectrum was consistent with the known constitution.

Fraction C was chromatographed on silica gel. The eluent was tetrachloromethane-methylene chloride (1:2), to which ethyl acetate (0.5 — 10 %) was gradually added. Two crystalline compounds were obtained.

8(S)-9-Acetoxy-O-senecioyl-8,9-dihydrooroselol (III), m.p. 126 — 126.5° (methylene chloride-petroleum ether), $[\alpha]_D+{}^{20}2°$ (c 0.6, CH_3OH), $[\alpha]_D^{20}-48°$, $[\alpha]_{578}^{20}-51°$ (c 1.2, $CHCl_3$) (Ref. 6, m.p. 123°, $[\alpha]_{578}^{24}-45°$ (c 2.3, $CHCl_3$)). The analytical data were concordant with the composition $C_{21}H_{22}O_7$. The ^{1}H NMR-data were identical with those reported by Bohlmann and Grenz.[6] For peucenidin (X),[4] m.p. 124.5 — 125.5°, $[\alpha]_D^{20}-46°$ (c 1, $CHCl_3$) was reported. The IR-data reported for (X)[4] and the ^{1}H NMR-spectrum[5] were similar to those obtained from (III).

8(S)-9-Acetoxy-O-isovaleryl-8,9-dihydrooroselol (IV), m.p. 88 — 88.5° (ether-petroleum ether), $[\alpha]_D^{20}+49°$ (c 0.6, CH_3OH), $[\alpha]_D^{20}-0.9°$ (c 1.2, $CHCl_3$) (Found: C 65.02; H 6.26. Calc. for $C_{21}H_{24}O_7$: C 64.93; H 6.23). The ^{1}H NMR-spectrum was identical with that reported by Bohlmann and Grenz.[6]

Fraction D upon crystallization from benzene afforded oroselol (II), m.p. 155 — 156° (Ref. 3, m.p. 156 — 157°). The IR-spectrum was identical with that of a sample obtained by hydrolysis of athamantin with potassium hydrogen carbonate in 50 % ethanol.[4] The ^{1}H NMR-spectrum was consistent with the known constitution.

The mother liquor was chromatographed on silica gel, using benzene to which ethyl acetate (2 — 10 %) was gradually added as the eluent. Two crystalline compounds were obtained.

8(S)-9-Hydroxy-O-senecioyl-8,9-dihydrooroselol (V), m.p. 132 — 135° (methylene chloride-petroleum ether), $[\alpha]_D^{20}+113°$ (c 0.6, CH_3OH). (Found: C 66.13; H 6.00. Calc. for $C_{19}H_{20}O_6$: C 66.27; H 5.85).

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* Added in proof: The diastereomer of 2-isopropyl-3-hydroxy-5-bromo-2,3-dihydrobenzofuran earlier denoted *trans*[14] has recently been shown to possess the relative configuration *cis*, by X-ray analysis (L. H. Zalkow, personal communication). Accordingly, the configurations 8(S),9(R) can safely be assigned to the coumarins (I), (III) — (VI) and XVI.

The ^{1}H NMR-data (CDCl$_3$, δ-values) are the following:

a. The coumarin moiety: H(3) 6.16 (1H, doublet); H(4) 7.63 (1H, doublet); $J_{3,4}=9.5$ cps; H(5) 7.37 (1H, doublet); H(6) 6.80 (1H, doublet); $J_{5,6}=8.5$ cps; H(8) 4.91 (1H, doublet); H(9) 5.65 (1H, multiplet or, when $-$OH is exchanged with $-$OD, doublet); $J_{8,9}=6.5$ cps; *gem*-dimethyl protons 1.74 and 1.82 (3H each, singlets); $-$OH group broad peak at *ca.* 3.6 (1H).

b. The senecioyl group: *gem*-dimethyl protons 1.87 and 2.13 (3H each, doublets) both $J=ca.$ 1 cps; vinylic proton 5.65 (1H, multiplet).

8(*S*)-9-isovaleryloxy-8,9-dihydrooroselol (VI), m.p. 138.5$-$139° (methylene chloride-petroleum ether) (Ref. 9 for vaginidin, m.p. 133$-$134°), [α]$_D^{20}+172°$ (*c* 0.4, CH$_3$OH). (Found: C 65.71; H 6.35. Calc. for C$_{19}$H$_{22}$O$_6$: C 65.88; H 6.40).

The ^{1}H NMR-data (CDCl$_3$, δ-values) are the following:

a. The coumarin moiety: H(3) 6.19 (1H, doublet); H(4) 7.63 (1H, doublet); $J_{3,4}=9.5$ cps; H(5) 7.44 (1H, doublet); H (6) 6.85 (1H, doublet); $J_{5,6}=8.5$ cps; H(8) 5.55 (1H, doublet); H(9) 6.99 (1H, doublet); $J_{8,9}=6.5$ cps; *gem*-dimethyl protons 1.42 (6H, singlet); $-$OH group 2.70 (1H, singlet).

b. The isovaleryl group: *gem*-dimethyl protons 0.95 (6H, multiplet); methylene group 2.20 (2H, multiplet); methine proton, hardly observable broad pattern *ca.* 2 (1H).

The ^{1}H NMR-spectrum was identical with the spectrum published for vaginidin.[8]

The root extract. In a way, similar to that described for the fruits, 500 g dried roots afforded 43 g of defatted extract, which was divided into the four main fractions A', B', C', and D'.

Fraction A' was rechromatographed on silica gel. The eluent was benzene to which ethyl acetate (0.5$-$8 %) was gradually added. 8(*S*)-*O*-isovaleryl-8,9-dihydrooroselol (VIII), m.p. 76.5$-$77.5° (ether-petroleum ether), [α]$_D^{20}+305°$ (*c* 0.4, CH$_3$OH) was obtained. (Found: C 69.23; H 6.77. Calc. for C$_{19}$H$_{22}$O$_5$: C 69.07; H 6.71). The IR-spectrum was identical with that of the sample prepared from authentic 8(*S*)-8,9-dihydrooroselol (XI) by acylation with isovaleric anhydride.

Fraction B' yielded athamantin (I), in all respects identical with the sample obtained from the fruits.

Fraction C' after rechromatography (as described for fraction C) yielded (IV), in all respects identical with the sample obtained from the fruits.

Fraction D'. Crystallization from benzene afforded oroselol (II) identical with that obtained from the fruits. The mother liquor contained small amounts of blue-fluorescent coumarins, which were not obtained in a pure state.

Preparation of 8(S)-O-senecioyl-8,9-dihydrooroselol (VII). 98 mg of 8(*S*)-8,9-dihydrooroselol (XI) were acylated according to Oppenauer[7] with an excess of senecioic anhydride/CaH$_2$, to which benzene was added, until the b.p. 110° was reached. The mixture was refluxed with stirring for 48 h, after which the starting material had disappeared (TLC), then cooled and poured into water with stirring. When the effervescence ceased, the mixture was extracted with ether. The ether phase was washed with sodium hydrogen carbonate solution, water, saturated sodium chloride solution, and dried. The residue, obtained by evaporation of the solvent, was purified by chromatography on silica gel. As eluents were used benzene-petroleum ether (3:1), benzene, and benzene to which ethyl acetate (1$-$8 %) was gradually added. 88 mg of the acylation product were obtained, m.p. 80$-$82° (ether-petroleum ether). [α]$_D^{20}+311°$ (*c* 0.3, CH$_3$OH). The ^{1}H NMR-spectrum was consistent with the assigned structure.

Preparation of 8(S)-O-isovaleryl-8,9-dihydrooroselol (VIII). 250 mg of 8(*S*)-8,9-dihydrooroselol (XI) were acylated with isovaleric anhydride as mentioned above for (VII). The yield was 240 mg of the acylation product, m.p. 76$-$77° (ether-petroleum ether) [α]$_D^{20}+309°$ (*c* 0.7, CH$_3$OH). The ^{1}H NMR-spectrum was consistent with the assigned structure.

Hydrogenolysis of 8(S)-9-acetoxy-O-senecioyl-8,9-dihydrooroselol (III). 100 mg of (III) in 96 % ethanol (40 ml) were hydrogenated at 30° with 50 mg of platinum oxide as a catalyst. After 100 min, when an amount of hydrogen corresponding to *ca.* 2 moles had been absorbed, the hydrogenation was interrupted, and the catalyst and solvent removed. The residue was chromatographed on silica gel, using as the eluent tetrachloromethane-methylene chloride (2:1) to which ethyl acetate (0.5$-$8 %) was gradually added. 31 mg of a hydrogenation/hydrogenolysis product were obtained, m.p. 76$-$77° (ether-petroleum ether), [α]$_D^{20}+306°$ (*c* 0.3, CH$_3$OH). The IR-spectrum was identical with that of (VIII).

Furthermore, 13 mg of hydrogenation product were isolated, m.p. 87—87.5° (ether-petroleum ether), $[\alpha]_D^{20}+49°$ (c 0.4, CH_3OH). The IR-spectrum was identical with that of (IV).

Hydrogenolysis of 8(S)-9-acetoxy-O-isovaleryl-8,9-dihydrooroselol (IV). 98 mg of (IV) were hydrogenated as above. The reaction was stopped after 110 min, when an amount of hydrogen corresponding to 1 mole had been absorbed. In addition to 12 mg of un-changed (IV) 25 mg of the hydrogenolysis product were obtained, m.p. 75.5—76.5° (ether-petroleum ether), $[\alpha]_D^{20}+290°$ (c 0.3, CH_3OH). The IR-spectrum was identical with that of (VIII).

Hydrogenolysis of 8(S)-9-isovaleryloxy-8,9-dihydrooroselol (VI). To a prereduced suspen-sion of platinum oxide (20 mg) in 2 ml of ethanol (96 %), 60 mg of (VI) were added. A stream of hydrogen was passed through at 0° for 4 h, after which the catalyst and solvent was removed. Column chromatography on silica gel, using as the eluent methylene chloride, to which acetone (0.5—2 %) was gradually added and preparative thin-layer chromatography on silica gel G using methylene chloride-acetone (85:15) as the eluent, afforded totally 16 mg of the starting material (VI) and 13 mg of 8(S)-8,9-dihydrooroselol (XI), m.p. 163—163.5° (methylene chloride-petroleum ether), $[\alpha]_D^{20}+268°$ (c 0.3, CH_3OH) (Ref. 16, m.p. 163.5—164°, $[\alpha]_D^{29}+273°$ (c 0.3, CH_3OH)). The IR-spectrum was identical with that of an authentic sample.

Acetylation of 8(S)-9-isovaleryloxy-8,9-dihydrooroselol (VI). 40 mg of (VI) were acety-lated with acetic anhydride/CaH_2 for 34 h using the procedure described above for the preparation of 8(S)-O-senecioyl-8,9-dihydrooroselol (VII). The reaction product was chromatographed on silica gel. As the eluent was used tetrachloromethane-methylene chloride (1:2), to which ethyl acetate (2—10 %) was gradually added. 28 mg of (XIII) were obtained, m.p. 119—120° (methylene chloride-petroleum ether), $[\alpha]_D^{20}+130°$ (c 0.3, CH_3OH). The ¹H NMR-spectrum was almost identical with that of (IV); their IR-spectra were distinctly different.

Acetylation of 8(S)-9-hydroxy-O-senecioyl-8,9-dihydrooroselol (V). 40 mg of (V) were treated with acetic anhydride-pyridine at room temperature for 4 h. The reaction mixture was poured into water and extracted with methylene chloride. The methylene chloride phase was washed with 1 N sulfuric acid, sodium hydrogen carbonate solution, water, and saturated sodium chloride solution, dried, and evaporated to dryness. Chromatog-raphy on silica gel, using tetrachloromethane-methylene chloride (1:2), to which 2 % of ethyl acetate had been added, as the eluent, yielded 30 mg of (III), m.p. 125—126° (ether-petroleum ether), $[\alpha]_D^{20}-49°$ (c 0.8, CH_3OH). The IR-spectrum was identical with that of natural (III).

Acetylation of 8(S)-8,9-dihydrooroselol (XI). A mixture of (XI) (50 mg), sodium acetate (100 mg), and acetic anhydride (0.6 ml) was heated to 120° in a closed tube for 30 h. The cooled reaction mixture was poured into water and extracted with ether. The ether phase was washed with sodium hydrogen carbonate solution, water, and saturated sodium chloride solution, dried, and evaporated to dryness. The yield of the acetylation product (XIV) was 40 mg, m.p. 135—136° (methylene chloride-petroleum ether), [Ref. 17, 127.5—128.5° (Kofler block)]. The ¹H NMR-spectrum was consistent with the assigned structure.

Acetylation of oroselol (II). 200 mg of oroselol were treated with acetic anhydride/CaH_2 for 24 h using the procedure described above for the preparation of 8(S)-O-senecioyl-8,9-dihydrooroselol (VII). The reaction mixture was cooled and worked up in the usual way. The crude acetylation product (228 mg), which crystallized on evaporation of the solvent, contained, in addition to the acetylation product, only trace amounts of the starting material (II) and the elimination product oroselone (TLC). Crystallization from methanol afforded oroselol acetate, m.p. 149—151° (Ref. 18, 149—151°). The ¹H NMR-spectrum was consistent with the assigned structure.

Alkaline methanolysis of 8(S)-9-acetoxy-O-senecioyl-8,9-dihydrooroselol (III). According to the method used by Prokopenko [4] for peucenidin, 100 mg of (III) were treated with 2.8 ml of a 0.4 % methanolic solution of sodium hydroxide at 50° for 5 h. The reaction mixture was worked up as usual and examined by thin-layer chromatography on silica gel GF_{254} (Merck) using petroleum ether-acetone (4:1) as the eluent. The following spots, mentioned in the order of increasing polarity, were observed: a yellow-fluorescent spot, which cochromatographed with oroselol methyl ether; a blue-fluorescent spot presumably corresponding to compound (XVII); a blue-fluorescent spot, which cochromatographed with the starting material; in addition, small amounts of more polar compounds were

present. These compounds in the solvent system methylene chloride-methanol (19:1) separated into a blue-fluorescent spot, a yellow-fluorescent spot cochromatographing with oroselol and finally a blue-fluorescent spot. No spot cochromatographing with oroselol acetate (yellow-fluorescent) was observed.

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